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(12) Patent:

(11) CA 740042

(54) POLYVINYL CHLORIDE STABILIZER

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ABSTRACT:

CLAIMS: [Show all claims](#)

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

(72) Inventors (Country):	WILLIAM E. LEISTNER (Not Available) OLGA H. KNOEPKE (Not Available) ARTHUR C. HECKER (Not Available)
(73) Owners (Country):	ARGUS CHEMICAL CANADA LIMITED (Not Available)
(71) Applicants (Country):	
(74) Agent :	
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N/A

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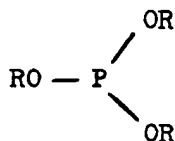
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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A polyvinyl chloride resin composition having improved resistance to discoloration when heated at elevated temperatures, comprising from 1.5% to 5% by weight of the resin of a compatible phosphite ester stabilizer having the formula:

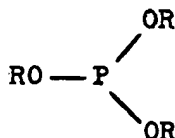


in which the R's are organic hydrocarbon radicals selected from the group consisting of alkyl radicals having from about four to about twelve carbon atoms, and phenyl and mixed alkyl phenyl radicals having from about seven to about fourteen carbon atoms, from one to two of the R's being alkyl, and from one to two of the R's being selected from the group consisting of phenyl and alkyl phenyl.

2. A polyvinyl chloride resin composition in accordance with claim 1, in which the phosphite is an octyl diphenyl phosphite.

3. A polyvinyl chloride resin composition in accordance with claim 1, in which the phosphite is a dioctyl phenyl phosphite.

4. A polyvinyl chloride resin composition having improved resistance to discoloration when heated at elevated temperatures, comprising from 1.5% to 5% by weight of the resin of a compatible phosphite ester stabilizer having the formula:

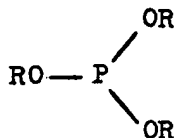


in which the R's are organic hydrocarbon radicals selected from the group consisting of alkyl radicals having from about four to about twelve carbon atoms, and phenyl and mixed alkyl phenyl radicals having from about seven to about fourteen carbon atoms, from one to two of the R's being alkyl, and from one to two of the R's being selected from the group consisting of phenyl and alkyl phenyl, and having from about 2 to about 10% by weight of the resin of an ester of an epoxy aliphatic fatty acid having from about twelve to about twenty-two carbon atoms and an aliphatic alcohol having up to about eight carbon atoms.

5. A polyvinyl chloride resin composition in accordance with claim 4, in which the ester is epoxidized soybean oil.

6. A polyvinyl chloride resin composition in accordance with claim 4, in which the phosphite is an octyl diphenyl phosphite.

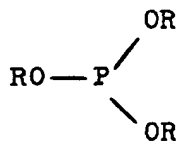
7. A polyvinyl chloride resin composition having improved resistance to discoloration when heated at elevated temperatures, comprising from 1.5 to 5% by weight of the resin of a compatible phosphite ester stabilizer having the formula:



in which the R's are organic hydrocarbon radicals selected from the group consisting of alkyl radicals having from about four to about twelve carbon atoms, and phenyl and mixed alkyl phenyl radicals having from about seven to about fourteen carbon atoms, from one to two of the R's being alkyl, and from one to two of the R's being selected from

the group consisting of phenyl and alkyl phenyl, and from about 0.02% to about 0.3% by weight of the resin of a metal salt selected from the group consisting of zinc, cadmium, tin and copper salts of an organic acid having from about six to about eighteen carbon atoms.

8. A polyvinyl chloride resin composition having improved resistance to discoloration when heated at elevated temperatures, comprising from 1.5% to 5% by weight of the resin of a compatible phosphite ester stabilizer having the formula:



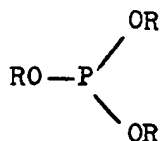
in which the R's are alkyl radicals having from about four to about twelve carbon atoms, and from about 0.5% to about 2% by weight of the resin of an alkyl phenol having from fourteen to thirty carbon atoms.

9. A polyvinyl chloride resin composition in accordance with claim 8, which also includes from about 2 to about 10% by weight of the resin of an ester of an epoxy aliphatic fatty acid having from about twelve to about twenty-two carbon atoms and an aliphatic alcohol having up to about eight carbon atoms.

10. A polyvinyl chloride resin composition in accordance with claim 8, which also includes from about 0.02% to about 0.3% by weight of the resin of a metal salt selected from the group consisting of zinc, cadmium, tin and copper salts of an organic acid having from about six to about eighteen carbon atoms.

11. A polyvinyl chloride resin composition having

improved resistance to discoloration when heated at elevated temperatures, comprising from 1.5% to 5% by weight of the resin of a compatible phosphite ester stabilizer having the formula:



- in which the R's are organic hydrocarbon radicals selected from the group consisting of alkyl radicals having from about four to about twelve carbon atoms, and alkyl phenyl radicals having from about seven to about fourteen carbon atoms, from one to two of the R's being alkyl, and from one to two of the R's being selected from the group consisting of phenyl and alkyl phenyl, from about 2% to about 10% by weight of the resin of an ester of an epoxy aliphatic fatty acid having from about twelve to about twenty-two carbon atoms and an aliphatic alcohol having up to about eight carbon atoms, and from about 0.02% to about 0.3% by weight of the resin of a metal salt selected from the group consisting of zinc, cadmium, tin and copper salts of an organic acid having from about six to about eighteen carbon atoms.

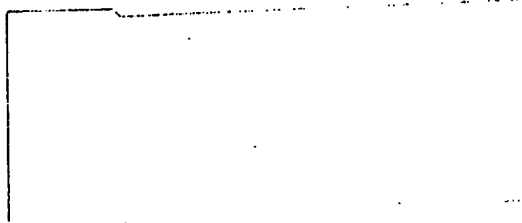
12. Polyvinyl chloride resin stabilized with 1.5% to 5 parts, per 100 parts of resin, of diphenyl mono-2-ethyl hexyl phosphite.

13. Polyvinyl chloride resin stabilized with 1.5% to 5 parts per 100 parts of resin, of di-2-ethyl hexyl monophenyl phosphite.

14. A composition of matter comprising a vinyl chloride resin and a stabilizer, said stabilizer comprising from 1.5% to 5 parts per 100 parts of resin of diphenyl mono-2-ethyl hexyl phosphite and from 2 to 10 parts per 100 parts

of resin of epoxidized soya bean oil.

15. A composition of matter comprising a vinyl chloride resin and a stabilizer, said stabilizer comprising from 1.5% to 5 parts per 100 parts of resin of di-2-ethyl hexyl monophenyl phosphite and from 2 to 10 parts per 100 parts of resin of epoxidized soya bean oil.



16. Polyvinyl chloride resin stabilized with 0.1 to 20 parts, per 100 parts of resin, of diphenyl mono-2-ethyl hexyl phosphite.

17. Polyvinyl chloride resin stabilized with 0.1 to 20 parts per 100 parts of resin, of di-2-ethyl hexyl mono-phenyl phosphite.

18. A composition of matter comprising a chlorine containing vinyl resin and a stabilizer, said stabilizer comprising from 0.1 to 20 parts per 100 parts of resin of diphenyl mono-2-ethyl hexyl phosphite and from 0.001 to 3 parts per 100 parts of resin of epoxidized soya bean oil.

19. A composition of matter comprising a chlorine containing vinyl resin and a stabilizer, said stabilizer comprising from 0.1 to 20 parts per 100 parts of resin of di-2-ethyl hexyl mono-phenyl phosphite and from 0.001 to 3 parts per 100 parts of resin of epoxidized soya bean oil.

20. A composition of matter comprising a chlorine containing vinyl resin and a stabilizer, said stabilizer comprising from 0.1 to 20 parts per 100 parts of resin of diphenyl mono-2-ethyl hexyl phosphite and a total of from 0.001 to 3.0 parts per 100 parts of resin of epoxidized soya bean oil, cadmium laurate and barium laurate.

This invention relates to stabilization of polyvinyl chloride plastics with a phosphorous acid ester containing an aliphatic component.

5 Triaryl phosphites have been proposed for stabilizing polyvinyl chloride plastics in U. S. Patent No. 2,572,571, issued to Marling on October 23, 1951. They have not proven satisfactory when used alone.

10 Aryl phosphite esters have been used extensively and alkyl and alkylaryl esters proposed as anti-clouding agents, to decrease haze in such plastics including metal salts as heat stabilizers in the proportion of 1 - 5 parts of the salts for 100 of the polyvinyl chloride, all as described in 15 U. S. Patent No. 2,564,646 issued to us on August 14, 1951.

20 We have now discovered the stabilization of polyvinyl chloride resins adequately for some purposes by the phosphite esters alone provided the proportion used is at least 1.5% of the weight of the polyvinyl chloride and provided the ester grouping contains at least one aliphatic component such as an alkyl or alkylene group.

25 When stabilization to meet all present commercial uses of polyvinyl chloride resins is to be effected, then we use the phosphite (1) alone or (2) with an epoxidized ester, an alkylphenol or both. When the phosphite and 30 epoxy compound are used jointly, there may be

*

and suitably is incorporated a catalytic proportion of a metal salt of a fatty acid in amount not more than 0.3 part for 100 parts of the resin to be stabilized.

5 When a salt of one of the said metals is used, it must be incorporated only in trace proportions not above 0.3 parts of the salt and the still smaller, calculated proportion of the actual metal.

10 Such low proportions of metal salt offer great advantages, including better heat sealing and printing properties of the stabilized plastic, no roll coating during processing, improved electrical properties of the finished material, outstanding transparency, or more glossy surface
15 than obtained heretofore. Also, products stabilized in this manner do not contain objectionable quantities of toxic metal ions.

20 We have found, for instance, that a sheeted plastic containing 100 parts of polyvinyl chloride (PVC), 45 parts dioctyl phthalate (DOP) plasticizer, and 3 of mono-octyl diphenyl phosphite discolored in 15 minutes heating at 350°F. only to a light yellow color, whereas the substitution of 3 parts of triphenyl phosphite, for the phosphite with the
25 octyl component, gave a plastic that turned to a deep brown color in the same test and in the same time.

30 We have found also that a PVC resin composition in which mono-octyl diphenyl phosphite, for example, is used in combination with epoxidized soya bean

oil or other non-volatile compatible epoxy compound will withstand 120 minutes heating at 350°F. with discoloration corresponding approximately to that of a comparable triphenyl phosphite and the same epoxy composition after only 30 minutes.

Using the phosphite ester containing an alkyl or an alkylene group or both with an epoxy compound, a trace proportion of a salt of one of the metals stated, and an alkyl phenol, we have made plastic sheets so resistant to discoloration on heating that, after 2 hours at 350° F., the test strips have substantially no color.

As to materials, the polyvinyl chloride resin may be any of the usual commercial forms including, for instance, polyvinyl chloride itself and copolymers of it with vinyl acetate, styrene, and maleate and fumarate esters, all with the vinyl chloride in predominating proportion. Examples of such resins that may be used are Geon 101 EP (polyvinyl chloride), Vinylite VYNW (copolymer of 96% vinyl chloride and 4% vinyl acetate), and a copolymer of 95% vinyl chloride with 5% diethyl maleate or fumarate.

The resin is ordinarily compounded with a usual proportion of a conventional plasticizer examples of which are dibutyl, dioctyl and didodecyl phthalate, sebacate, and adipate and tricresyl phosphate.

Our phosphite ester component of the stabilizer is a triester that is substantially non-volatile at ordinary temperatures, will dissolve in polyvinyl chloride during compounding operations, and will not separate therefrom during use of the finished product. The triester must contain at least 1 aliphatic group and may contain 2 or 3 such groups, examples of which are butyl, octyl, decyl, dodecyl, and the alkylene radicals of glycols such as ethylene, propylene and hexylene glycols, these hydrocarbon radicals being derivable from alcohols. In case an alkylene group is present, then a typical structure of the triester includes one alkylene group (replacing two hydrogens of phosphorous acid) and an alkyl or an aryl group replacing the third hydrogen.

Aryl groups that may be represented in the phosphite esters are phenyl, cresyl, octylphenyl, and homologs thereof.

In general, the triesters of kind used by us are represented by the type formula



in which at least one R is an aliphatic hydrocarbon group and the remaining R component may be either alkyl or aryl. Examples of such triesters of phosphorous acid that may be used and that illustrate

the class more particularly are monooctyl
diphenyl, dioctyl monophenyl, trioctyl,
monododecyl diphenyl, didodecyl monophenyl,
tridodecyl, monobutyl diphenyl, dibutyl
5 monocresyl, and monobutyl dioctylphenyl
phosphite, monooctyl propyleneglycol phosphite,
monophenyl propyleneglycol phosphite and
monophenyl 1,6-hexanediol phosphite. It
will be noted from these examples that two
10 alkyl groups in some of the triesters are
replaced by a single alkylene group.

If any of the phosphite triesters is
selected for use is not available commercially,
then the ester may be made by any conventional
15 published methods, the starting materials being
selected to provide in the finished triester
the desired hydrocarbon groups, all in
accordance with known technique.

As the epoxy compound we use a non-
20 volatile and PVC compatible compound, as, for
instance, the epoxidized ester of a higher
C₁₂-C₂₂ unsaturated fatty acid as, for example,
those acids found in natural fatty oils. The
acids may be used either in substantially pure
25 form or in mixtures such as the fatty acids of
soya bean, corn or cotton seed oil. A suitable
ester is the triglyceride, such as found in
the fatty oils named, or esters of the fatty
acids of these oils or of oleic acid with such
30 aliphatic monohydric alcohols as butyl, hexyl,

or octyl alcohol. Other epoxy compounds that may be used are the diglycidyl ether of bisphenol and EP 101 (3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexanecarboxylate).

The metal salt used in conjunction with the triesters of phosphorous acid and the said epoxidized ester must be a salt of zinc, cadmium, tin or copper. The acid radical of the salt may be that of any of the C_6-C_{18} organic acids. Examples of such acids that are used to advantage are caproic, 2-ethylhexoic, lauric, naphthenic, palmitic, stearic and benzoic acid.

When our phosphite esters used are exclusively alkyl esters, then alkylphenols are introduced to advantage to increase the stabilizing effect. Examples are dibutylresol, octyl, nonyl, and dodecyl phenols, and diamyl, dinonyl and didodecyl phenols and butylated hydroxyanisole. These substituted phenols are substantially non-volatile under conditions of use.

Proportions of the several components, showing the relationship of each, when used, to other members of the stabilizing composition, are given below on the basis of parts for 100 parts of the polyvinyl chloride resin. The conventional plasticizers, forming no part of this invention are taken in usual proportions, as for instance, 25-50 parts; even more may be used in making plastisol type products.

5 It is to be understood that the alkylphenol may be omitted entirely when the phosphite ester is in part an ester of a phenol, as in the case of a monoalkyl diphenyl phosphite or a dialkyl monoaryl phosphite.

	Component of Stabilizer	<u>Parts for 100 parts of PVC Resin</u>	
		Permissible Range	A Commercial Proportion
10	Triester of Phosphorous Acid	1.5 - 5	3
	Epoxy compound	2 - 10	5
	Alkylphenol	0.5 - 2	1
	Metal salt	0.02 - 0.3	0.02-0.2*

15 * Suitable commercial proportions of the salts of the several metals are 0.02-0.15 part for zinc, copper, and cadmium and 0.02-0.3 part for tin.

20 The trace proportion of the metal salt used is illustrated in the case of a typical salt such as zinc 2-ethylhexoate. In this salt the proportion of zinc is approximately 20%. The amounts of 0.02 - 0.1 part of the salt for 100 parts of PVC correspond, there-
 25 fore, to only about 0.004 - 0.02 of zinc metal.

It is significant that larger proportions of metal salts than 0.3 part for 100 of the PVC resin, when incorporated with the other three components of our stabilizer compositions
 30 do not cause decrease in heat discoloration of

the plastic but actually increase the discoloration. Thus the use of zinc 2-ethylhexoate in the proportion of 0.4 part for 100 of the vinyl resin, in conjunction with the other components of our composition, gave good color stability for a short time but a dark brown, practically black, plastic when a test strip was heated at 350°F. for 30 minutes. A control sample omitting the metal salt became only lemon yellow under the same circumstances. Another comparable sample containing only 0.025 parts of the zinc 2-ethylhexoate in 120 minutes heating at 350°F. showed no appreciable discoloration.

The conditions of compounding the vinyl chloride plastic are those that are common in this industry. Thus 100 parts of resin VYNW (96% vinyl chloride and 4% vinyl acetate copolymer) or 101 EP (all polyvinyl chloride) are mixed in a dry blender with the plasticizer, which in all the experiments here reported was dioctylphthalate (DOP) in the proportion of 45 parts. There are also incorporated the various components of the stabilizer composition in the proportions shown or to be shown in the subsequent examples. The whole mass is agitated by tumbling for a period of 1 hour, then transferred to a Banbury mixer, and fused for 10 minutes

at a temperature of approximately 300° F.
The whole is then placed on a warm-up mill
of roll temperatures also 300° F. and is
fed through this mill as needed, to a 3 or
5 4 roll calender of temperatures 280°-350°F.

The vinyl plastic so compounded is
sheeted off at a thickness of 0.004 inch
and cut into strips used for discoloration
and stability tests described herein. In
10 these stability tests, the sheeted plastics
are exposed to a temperature of 350° F. and
specimens removed at 15 minute periods up
to 2 hours.

The invention will be further illustrated
15 by description in connection with the following
specific examples of the practice of it. In
these examples and elsewhere herein proportions
are expressed as parts by weight.

EXAMPLE 1

20 The plastic was made of the following
composition:

	<u>Components</u>	<u>Parts</u>
	VYNW	100
	DOP	45
25	Monooctyl diphenyl phosphite	3

The sheeted product was substantially
colorless. After 30 minutes heating at 350°F.,
it was light amber in color and much lighter
30 than the brown developed with 3 parts of

triphenyl phosphite as the sole stabilizer.

EXAMPLE 2

The plastic was made of the following composition:

5	<u>Components</u>	<u>Parts</u>
	VYNW	100
	DOP	45
	Monooctyl diphenyl phosphite	3
10	Epoxidized soya bean oil (G-62)	5

The sheeted sample of this plastic, after 90 minutes testing at 350°F., was of lemon yellow color approximately equal to that in a comparable composition after only 15 minutes heating in which triphenyl phosphite had been used in place of the alkyl aryl phosphite.

EXAMPLE 3

20 The tabulated composition and the procedure of Example 2 were used except that the phosphite ester was trioctyl phosphite, an antioxidant (nonylphenol) was included in the proportion of 1 part, and
25 the epoxidized ester was Drapex 3.2 (epoxidized octyl ester of oleic acid). In this case the product, after 90 minutes heating, was white with only a light yellow tinge.

EXAMPLE 4

Here the composition was as follows:

	<u>Components</u>	<u>Parts</u>
	VYNW	100
5	DOP	45
	Epoxidized soya bean oil	5
	Tridodecyl phosphite	3
	Di-t-butylparacresol	1
	Zinc 2-ethylhexoate	0.025
10	Discoloration in 120 minutes at 350°F. was negligible.	

EXAMPLE 5

Excellent results as to color stability were obtained also by the separate use, in compositions such as that of Example 4, of 0.03 part of copper benzoate, 0.125 part of cadmium 2-ethylhexoate, and 0.2 part of tin benzoate, in place of the zinc salt.

EXAMPLE 6

The procedure of any of the Examples 1-5 is followed with the substitution of the alkyl group of the phosphorous acid ester by any of the other aliphatic groups disclosed herein on an equivalent weight basis, with the substitution of any of the antioxidants disclosed herein on an equal weight basis for the particular alkyl phenol used, and the substitution of any of the epoxy compounds disclosed for the epoxidized ester selected for any particular Example.

Also the members of any class of components may be used in mixtures with others of the same class.

5 It is to be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

DERWENT-ACC-NO: 1968-66581P

DERWENT-WEEK: 196800

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TITLE: Polyvinyl chloride resin resistant to discoloration by

PATENT-ASSIGNEE: ARGUS CHEM CANADA LTD [ARGU]

PRIORITY-DATA: 1956US-0584891 (May 15, 1956)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES
MAIN-IPC			
CA 740042 A		N/A	000 N/A

ABSTRACTED-PUB-NO: CA 740042A

BASIC-ABSTRACT:

The resin contains 1.5-5% wt. of a phosphite ester stabilizer of formula:- in which 1 or 2 of the R's are C4-12 alkyl radicals, and the remainder are C6-14 phenyl or alkyl phenyl radicals. The resin may also contain 2-10% wt. of an ester of a C12-22 epoxy aliphatic fatty acid and a C1-8 aliphatic alcohol, 0.5-2% wt. of a C14-30 alkyl phenyl, and 0.02 - 0.3% wt. of a Zn, Cd, Sn or Cu salt of a C6-18 organic acid. The phosphite is preferably octyl diphenyl phosphite, dioctyl phenyl phosphite, diphenyl 2-ethyl hexyl phosphite, or di-2-ethyl hexyl phenyl phosphite, and the ester is epoxidised soya bean oil.

DERWENT-CLASS: A00

CPI-CODES: A04-E02; A08-A04;

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Basic Abstract Text - ABTX (1):

The resin contains 1.5-5% wt. of a phosphite ester stabilizer of formula:- in which 1 or 2 of the R's are C4-12 alkyl radicals, and the remainder are C6-14 phenyl or alkyl phenyl radicals. The resin may also contain 2-10% wt. of an ester of a C12-22 epoxy aliphatic fatty acid and a C1-8 aliphatic alcohol, 0.5-2% wt. of a C14-30 alkyl phenyl, and 0.02 - 0.3% wt. of a Zn, Cd, Sn or Cu salt of a C6-18 organic acid. The phosphite is preferably octyl diphenyl phosphite, dioctyl phenyl phosphite, diphenyl 2-ethyl hexyl phosphite, or di-2-ethyl hexyl phenyl phosphite, and the ester is epoxidised soya bean oil.

Title - TIX (1):

Polyvinyl chloride resin resistant to discoloration by

Standard Title Terms - TTX (1):

POLYVINYL CHLORIDE RESIN RESISTANCE DISCOLOUR